Mössbauer Spectra of Various Organic Iron Chelates

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(Received February 25, 1965)

In a previous paper,[1] the Mössbauer spectra of various inorganic iron compounds were studied and some significant aspects of the spectra were discussed. The results showed that such an investigation can give valuable information concerning the change in the charge distribution in the molecule as a function of the chemical structure or bindings.

In the studies reported on in this paper, the work on the Mössbauer spectra was extended to a variety of organic iron chelates. The choice of organic iron chelates as an absorber was made because a series of structurally-related compounds are readily available and because various kinds of bindings are included in the organic iron chelates.

The two parameters of major interest, the isomer shift and the quadrupole splitting, will be discussed, as will the correlation between the above values and the molecular structure. Special attention will be paid to the effect on the isomer shift of varying ligands bonded to the iron atom.

Experimental

Apparatus and Procedure. — The apparatus and procedure employed were essentially the same as those described in the previous paper.[1] All measurements were made at room temperature and with respect to a ^{57}Co source diffused into metallic copper. The isomer shifts were referred to the stainless steel absorber.

Minor variations in technique were matters of convenience in the cases of hygroscopic and light-sensitive substances. Such samples were stored under a vacuum in the dark until they were mounted to the absorber disk. The mounted samples were then covered with a piece of black paper and adhesive tape to avoid light and moisture respectively.

Materials. — Most of the chemicals used were commercial reagent-grade products which were used without any further purification. (The Mössbauer effect is not very sensitive to a small impurity.) Several samples were prepared in the laboratory because of the lack of commercial ones. Two

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[1] Y. Takashima and S. Ohashi, This Bulletin, 38, 1684 (1965).

samples, bis(salicylaldehyde)ethylenediimine iron(III) chloride and oxide, were provided by Professor Tamotsu Yoshino of Kyushu University.

The commercially-obtained samples were the following:

Monosodium-ethylenediaminetetraacetato-iron(III), (Na·Fe-EDTA), iron(III)-nitrilotriacetate, (Fe(III)-NTA), iron(III)-acetylacetonate, {Fe(III)-$(AA)_3$}, iron(III)-trifluoroacetylacetonate, {Fe(III)-$(TAA)_3$}, iron(III)-thenoyltrifluoroacetonate, {Fe(III)-$(TTA)_3$}.

The above chemicals were obtained from Dojin Pharmaceutical Laboratories, Kumamoto. All the other chemicals, shown below, were purchased from Wako Pure Chemical Industries, Ltd., Osaka:

Iron(III) formate $\{Fe(HCO_2)_3 \cdot H_2O\}$, iron(III) succinate $\{Fe_2(C_3H_4O_4)_3\}$, iron(III) tartrate $\{Fe_2(C_4H_4O_6)_3 \cdot H_2O\}$, iron(III) malate $\{Fe_2(C_4H_4O_5)_3\}$, iron(III) citrate $\{FeC_6H_5O_7 \cdot 5H_2O\}$ ammonium iron(III) citrate $\{(NH_4)_3[Fe(C_6H_5O_7)_2]\}$, basic iron(III) benzoate $\{[Fe_3(C_6H_5COO)_6 \cdot (OH)_2](OH)\}$, iron(II) oxalate $(FeC_2O_4 \cdot 2H_2O)$, iron(II) lactate $\{Fe(C_3H_5O_3)_2 \cdot 3H_2O\}$, iron(II) gluconate $\{Fe(C_3H_6O_4)\}$, iron(II) tartrate $(FeC_4H_4O_6 \cdot H_2O)$.

The following samples were prepared in the laboratory. The preparation techniques were based on " Gmelins Handbuch der anorganishen Chemie " in most cases. Trisalicylaldehyde-diimine iron(III), phenylnitrosohydroxylamine-iron(III) oxide and phenylnitrosohydroxylamine iron(III) were made by Tsumaki's method.[2]

Iron(III) Acetate A. — Wet iron(III) hydroxide containing 10% iron was dissolved in 95% acetic acid. The solution was then allowed to stand over concentrated sulfuric acid in a vacuum desiccator for several days until the precipitate appeared.

Iron (III) Acetate B. — Wet iron(III) hydroxide containing 20% iron was dissolved in pure acetic acid. The following procedures were the same as those described above.

Iron(III)+Cr(III) Acetate (Cr : Fe=1 : 2 and 2 : 1). —These compounds were prepared in a way similar to that described in the case of iron(III) acetate A. However, the initial hydroxides used were mixed hydroxides of iron(III) and chromium(III) having ratios (atom) of 1 : 2 and 2 : 1.

Iron(III) Salicylate. — To 50 ml. of an aqueous solution of 4.8 g. of sodium salicylate, 40 ml. of ether and 50 ml. of an aqueous solution of 2.7 g. iron(III) chloride were added. After the mixture had stood for several hours, the red precipitate formed was filtered. The precipitate was dried over calcium chloride.

1,10-Phenanthroline Iron(II) Chloride, $\{(Phen)_3Fe\}Cl_2 \cdot 7H_2O$.—Ethanolic solutions of both 1,10-phenanthroline and iron(II) chloride were mixed. The precipitate was obtained by the addition of acetone. The resultant red precipitate was recrystallized from a small amount of water.

1,10-Phenanthroline Iron(III) Chloride, $[(Phen)_2Fe(OH)_2Fe(Phen)_2]Cl_4$. — The method of preparation was essentially the same as that described above. The only exception was the use of iron(III) chloride instead of iron(II) chloride.

Hexaureo-iron(III) Chloride, $\{[Fe(CON_2H_4)_6]Cl_3 \cdot 3H_2O\}$.[3]—Concentrated iron(III) chloride and urea solutions were mixed. The mixture was then evaporated in a vacuum desiccator containing sulfuric acid until the precipitate was produced.

Potassium Iron(III) Diglycolate, $\{K[Fe(CH_2O \cdot COO)_2] \cdot H_2O\}$.[4]—To 2 ml. of a 1 M iron(III) chloride solution was added 40 ml. of a 2 M potassium glycolate solution. The addition of alcohol to the mixture yielded a pale green precipitate.

Iron(III) Oxalate, $Fe_2(C_2O_4)_3$. — Iron(III) nitrate and oxalic acid were dissolved in 65% nitric acid to saturation. The yellow solution thus obtained was then let stand over sulfuric acid in a vacuum desiccator until the precipitate was formed.

Bis(quinaldinato) Iron(II), $\{Fe(C_{10}H_6O_2N)_2\}$. — Iron(II) chloride (5 g.) was added to 50 ml. of an aqueous solution made up with 10 g. of quinaldic acid. A red precipitate was formed almost immediately. After the mixture had stood for several hours, the color of the precipitate changed from red to purple. This purple precipitate (cis form) was used for the Mössbauer measurement.

Results and Discussion

The isomer shifts and the quadrupole splittings obtained for a variety of organic iron compounds are summarized in Table I.

The magnitudes of the isomer shift can, in principle, be related to the details of the bonding between iron and the ligands; i.e., the isomer shifts decrease regularly with the increasing covalency. In this connection, we indicated in the previous paper[1] that even atoms well separated from the iron affect the isomer shift.

The general tendency to be noticed from Table I is that the compound of more complicated chemical structures show the larger values of the isomer shift and of the quadrupole splitting within the series of chemically-related compounds.

Comparing the results for the isomer shifts and the quadrupole splittings for a series of iron-carboxylic acid compounds, it can be interpreted that the simpler compounds have a more covalent tendency in their bonds between the iron atom and carboxylic acid groups.

It was noted that[5] there was negligible quadrupole splitting in the case of the ionic ferric compound because of its $3d^5$ electron configuration. However, in almost all the organic iron chelates investigated, splitting did occur. This probably was caused by the field gradient from the neighboring atoms rather than by the iron atom itself. Presumably, the magnitude of the quadrupole splitting can be a measure of the crystallographic asymmetry.

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[2] T. Tsumaki, *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaishi*), **55**, 1245 (1934).

[3] G. A. Barbieri, *Chem. Zent.*, **84**, 1035 (1913).

[4] Ad. Paira, *Ber.*, **47**, 1773 (1914).

[5] S. DeBenedetti, G. Lang and R. Ingalls, *Phys. Rev. Letters*, **6**, 60 (1961).

TABLE I. ISOMER SHIFT, δ AND QUADRUPOLE SPLITTING, ε, OF VARIOUS ORGANIC IRON COMPOUNDS

Compound		δ, mm./sec.	$\varepsilon=\frac{1}{4}e^2qQ$ mm./sec.
$Fe(HCO_2)_3 \cdot H_2O$	Iron(III) formate	+0.32	0.17
$[Fe_3(CH_3COO)_6(OH)_2]CH_3COO$	Iron(III) acetate A (Basic)	+0.46 +0.44	0 0.33
$[Fe_3(CH_3COO)_6](CH_3COO)_3$	Iron(III) acetate B	+0.46 +0.44	0 0.36
$[Fe_2Cr(CH_3COO)_6(OH)_2]CH_3COO$		+0.47 +0.43	0 0.33
$[FeCr_2(CH_3COO)_6(OH)_2]CH_3COO$		+0.44	0.27
$K[Fe(CH_2OCO_2)_2] \cdot H_2O$	Potassium-iron(III) diglycolate	+0.52	0.15
$Fe_2(C_2O_4)_3 \cdot 5H_2O$	Iron(III) oxalate	+0.36	0
$(NH_4)_3[Fe(C_2O_4)_3] \cdot 3H_2O$	Ammonium tris(oxalato) ferrate(III)	Absorption not observed	
$K_3[Fe(C_2O_4)_3]$	Potassium tris(oxalato) ferrate(III)	Absorption not observed	
$Fe_2(C_3H_4O_4)_3$	Iron(III) succinate	+0.39	0.20
$Fe_2(C_4H_4O_6)_3$	Iron(III) tartrate	+0.44	0.25
$Fe_2(C_4H_4O_5)_3$	Iron(III) malate	+0.45	0.25
$FeC_6H_5O_7 \cdot 5H_2O$	Iron(III) citrate	+0.56	0.16
$(NH_4)_3Fe(C_6H_5O_7)_2$	Iron(III) ammonium citrate	+0.49	0.55
$[Fe_3(C_6H_5COO)_6(OH)_2]OH$	Iron(III) benzoate	+0.36 +0.53	0 0.33
$[Fe_3(C_6H_5OHCOO)_6(OH)_2\text{-}C_6H_5OHCOO \cdot 3H_2O$	Iron(III) salicylate	+0.49 +0.51	0.16 0.55
$Fe(C_2O_4) \cdot 2H_2O$	Iron(II) oxalate	+1.32	1.03
$Fe(C_3H_5O_3)_2 \cdot 3H_2O$	Iron(II) lactate	+1.20	1.39
$Fe(C_3H_6O_4)$	Iron(II) gluconate	+1.08	1.30
$Fe(C_4H_4O_6) \cdot H_2O$	Iron(II) tartrate	+1.47	1.31
$Fe(C_{10}H_6O_2N)_2$	Bis(quinaldinato) iron(II)	+1.09	1.24
Na·Fe(III)-EDTA	Monosodium iron(III) ethylenediamine tetraacetate	−0.16 +0.60	0 0
Fe(III)-NTA	Iron(III) nitrilotriacetate	+0.41	0
$[C_{16}H_{14}O_2N_2Fe]_2O$	Bis(salicylaldehyde) ethylenediimine iron(III) oxide	+0.46	0.40
$[C_{16}H_{14}O_2N_2Fe]Cl$	Bis(salicylaldehyde) ethylenediimine iron(III) chloride	+0.54	0.71
$(C_{21}H_{15}O_3N_2Fe)(C_6H_5O_2)$	Tris(salicylaldehydediimine iron(III)+nitrobenzene	+0.61	0.18
$[(Phen)_3Fe^{II}]Cl \cdot 7H_2O$	1,10-Phenanthroline iron(II) chloride	+0.29	0
$[(Phen)_2Fe(OH)_2Fe(Phen)_2]Cl_4$	1,10-Phenanthroline iron(III) chloride	+0.64	0.41
$Fe(III)\text{-}(AA)_3$	Iron(III) acetylacetonate	Absorption not observed	
$Fe(III)\text{-}(TAA)_3$	Iron(III) trifluoroacetylacetonate	Absorption not observed	
$Fe(III)\text{-}(TTA)_3$	Iron(III) thenoyltrifluoroacetonate	Absorption not observed	
$[Fe(CON_2H_4)_6]Cl_3 \cdot 3H_2O$	Hexaureo-iron(III) chloride	Absorption not observed	
$(C_{12}H_{10}O_4Fe)_2O$	Phenylnitrosohydroxylamine-iron(III) oxide	Absorption not observed	
$(C_6H_5O_2N_2)_3Fe$	Phenylnitrosohydroxylamine-iron(III)	Absorption not observed	

Considering all of the above concepts, we are now in a position to discuss some characteristics in each particular spectrum.

Iron(III) Oxalate.—The iron atoms in $Fe_2(C_2O_4)_3 \cdot 5H_2O$, $K_3[Fe(C_2O_4)_3]$ and $(NH_4)_3[Fe(C_2O_4)_3]$ have been considered to be located in similar chemical environments. Nevertheless, the latter two compounds showed no absorption, while the former displayed a single absorption peak at room temperature. Unfortunately, it is hardly possible at present to make a detailed discussion. However, one possible interpretation is that there may be different types of iron atoms in these compounds; i. e., the one shows absorption, but the other does not for some unidentified reason. Suppose we write the molecular formula as $Fe^*[Fe(C_2O_4)_3]\cdot 5H_2O$ instead of $Fe_2(C_2O_4)_3\cdot 5H_2O$, the asterisked iron atom differing in its binding mode from the other iron atom. This situation may be favorably compared with that of iron(III) chromate discussed in the previous paper.[1] Experiments to elucidate this assumption need to be conducted at a lower temperature. The chemical ascertainment of the structure of iron oxalate is also needed.

Iron(III) Acetates and Iron(III) Benzoate.—The spectra of these compounds have triple absorption peaks. They may be resolved either into two single lines or into one doublet and one single line. We tried out both analyses and felt that the latter is more reasonable. Thus, the spectrum was interpreted as the superposition of a quadrupole split and a single line. This may naturally be explained by the presence of different types of iron atoms in these compounds as a result of their polynuclear structure. For example, the spectrum and a generally-adopted structural formula of iron(III) acetate A are given in Figs. 1a and 1b:

The components of the composite spectra are shown by the broken line. The first analysis, shown in Fig. 1a, does not support the structure described above, because the split peak should be assigned to the central iron atom in view of its intensity. This fact is inconsistent with the general rule that a central atom is in a more symmetrical environment than are outside atoms. This difficulty was overcome by using the other analysis, shown in Fig. 1b, where two outer lines correspond to the quadrupole splitting due to two "outside" iron atoms and the central single line assigned to a central iron atom.

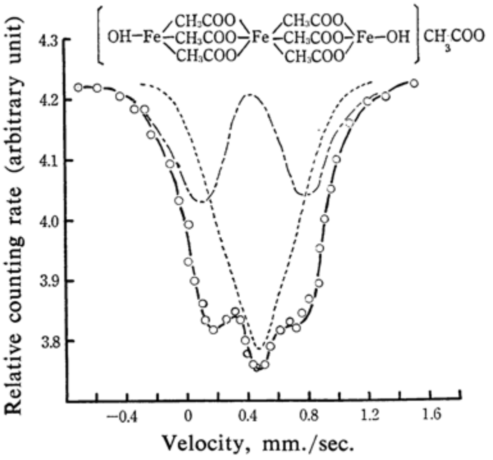

Fig. 1a. Mössbauer spectrum of iron(III) acetate A.

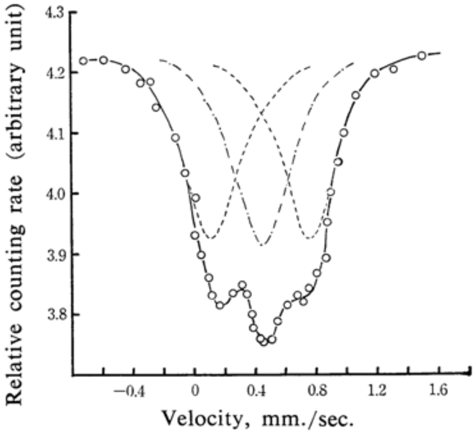

Fig. 1b. Mössbauer spectrum of iron(III) acetate A.

The spectra for iron(III) acetate A and B were almost identical. The minor difference observed must have arisen from the slightly different molecular structures of these acetates.

A particularly instructive case was the comparison of the spectra obtained for iron(III)+chromium(III) acetates with that obtained previously for iron(III) acetate A. The middle single peak was slightly decreased in intensity in the case of the mixed acetate (Fe : Cr = 2 : 1), and it disappeared almost completely in the case of the other mixed acetate (Fe : Cr = 1 : 2), while the outer double peaks remained essentially unchanged in shape. This fact could be interpreted qualitatively as meaning that chromium atoms can occupy any iron sites in the molecule, while the resultant distribution of chromium is not uniform but one-sided.

Iron(III) Salicylates.—The Mössbauer spectrum of this compound showed four resonance

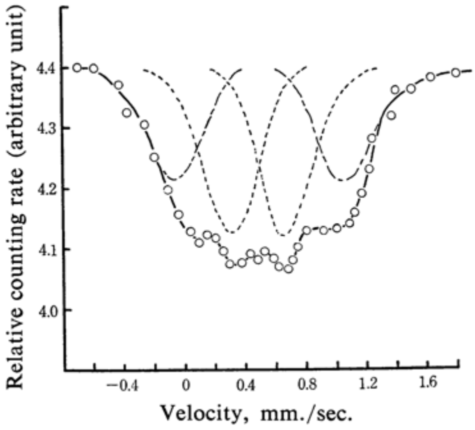

Fig. 2. Mössbauer spectrum of iron(III) salicylate.

absorption maxima (Fig. 2). The spectrum was analyzed by assuming that the quadrupole pair were of equal intensity. Thus, it was concluded that this spectrum is resolved into two doublets (dotted curves), the middle one showing an isomer shift of 0.49 mm./sec., while that for the outer one is 0.51 mm./sec. The measured values of the quadrupole splitting of the middle and outer doublets are 0.17 and 0.55 mm./sec. respectively. By assuming a trinuclear structure for the compounds, both the outside and central iron atoms can be considered to be situated at a point where the electric field gradient is nonzero.

Na·Fe(III)-EDTA, Fe(III)-NTA.—The spectra of these compounds showed main single peaks at +0.60 and +0.41 mm./sec. respectively. This fact indicates that the bondings are primarily ionic and that the iron atoms are in an octahedral symmetry. This conclusion is not in agreement with that of a previous infrared spectroscopic study,[6] in which the bonding between iron and EDTA has been reported to be covalent. It seems possible that this disagreement may be ascribed to an ambiguous definition of terms, ionic and covalent.

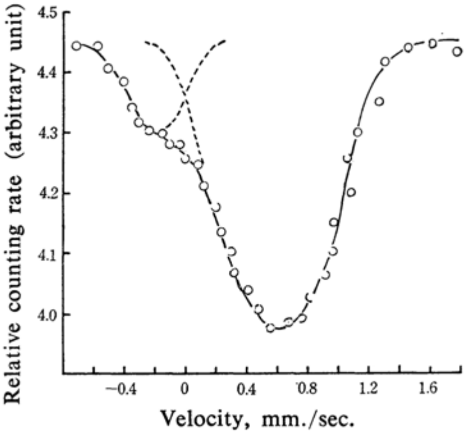

Fig. 3. Mössbauer spectrum of Na·Fe(III)-EDTA.

One peculiar anomaly of the spectrum was observed in the case of the Fe(III)-EDTA sample. As is shown in Fig. 3, the spectrum exhibited considerably more line broadening than other typical spectra. In addition, a shoulder appeared at −0.16 mm./sec. This shoulder can not be readily explained, but it could possibly be attributed to some impurity which has a strong covalent character. The investigation of this possibility must be the subject of future research.

Bis(salicylaldehyde)ethylenediimine Iron(III) Chloride and Oxide. — As may be seen from Fig. 4, these two compounds are closely related in chemical structure. Accordingly, no large differences in the isomer shift and quadrupole splitting were expected between them. Nevertheless, the experimental observations showed relatively large differences in their magnitude. This fact must be attributed to the molecular architecture of these compounds. In this connection we should note that, in a book by Martell and Calvin[7] on the chemistry of the metal chelate compound, they mentioned that the cobalt chelate of salicylaldehyde ethylenediimine crystallizes in layers, with holes running through the layers. The results of our Mössbauer study of the iron chelates also support the view of such a planar structure of the compounds. The oxygen or chlorine atoms may be interposed between two closely adjacent pairs of the unit cell, so that they behave as an atom covalently bonded to two adjacent iron atoms. The electronic charge distribution around the iron atoms which determine the isomer shift and quadrupole splitting can be considerably affected by the oxygen or chlorine in the molecule because of their high electronegativity.

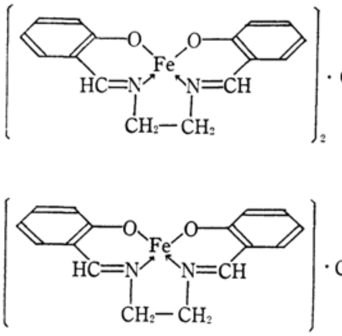

Fig. 4. Structural formulas of bis(salicylaldehyde)ethylenediimine iron(III) chloride and the oxide.

1, 10-Phenanthroline Iron(II) Chloride.—This compound, which is regarded as a very stable covalent compound, showed a small isomer shift, suggesting greater covalency, whereas the relatively unstable iron(III) compound of 1, 10-phenanthroline shows a large isomer shift, suggesting a small covalent contribution. Since the bonding arrangement of the former compound resembles that of the ferrocyanide complex, the spectrum showed a single peak.

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[6] D. T. Sawyer and J. M. McKinnie, *J. Am. Chem. Soc.*, **82**, 4191 (1960).

[7] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc. Englewood Cliffs, N. J. (1956), pp. 270, 342.

On the contrary, the latter displayed a double-peaked spectrum which may have arisen from the binuclear structure of the molecule.

Divalent Iron Organic Compounds.—Table I includes the values of the isomer shift and quadrupole splitting for several divalent iron compounds. The magnitude of these values were, of course, far larger than those of trivalent iron compounds. However, the present data may not be very accurate because of instrumental limitations; i. e., our instrument is not designed for a wide-range Doppler velocity, but is, rather, most useful in the neighborhood of zero velocity covering the ±1.0 mm./sec. range. For this reason, these data will not be further discussed here.

Compounds Whose Resonance Absorption was not Observed at Room Temperature. — In our observation, there are several iron-bearing organic compounds that did not show any resonance absorption. The chemical structures of the compounds studied are shown in Fig. 5.

All these compounds are characteristic in their binding nature; i. e., in all cases an iron atom is coordinated with oxygen atoms. There is no a priori reason why the resonance absorption does not occur in these compounds.

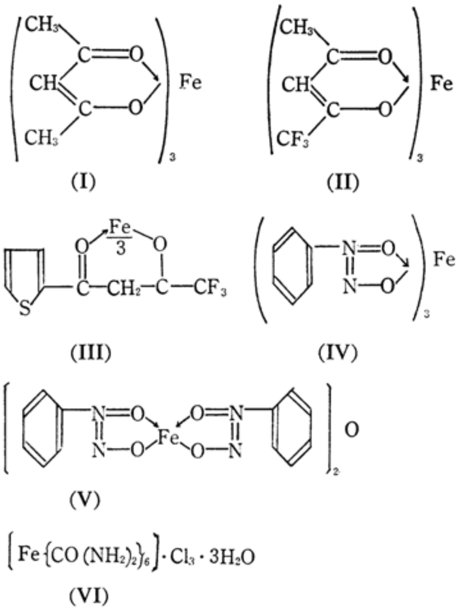

Fig. 5. Structural formulas of some organic iron(III) chelates.
(I) Iron(III) acetylacetonate
(II) Iron(III) trifluoroacetylacetonate
(III) Iron(III) thenoyltrifluoroacetonate
(IV) Phenylnitrosohydroxylamine-iron(III)
(V) Phenylnitrosohydroxylamine-iron(III) oxide
(VI) Hexaureo-iron(III) chloride

In any event, however, the absence of the Mössbauer effect should be attributed to either the low Debye temperature or the high recoil probability of the compound. Nevertheless, although such data for these organic compounds are not available at present, our speculation would prefer the interpretation that the disappearence of the absorption is caused by the latter.

It should be noted that the Mössbauer effect was not observed in the case of a dry cation exchanger (Dowex 50) saturated with iron(III) ions (thickness=∼10 mg. Fe/cm^2). The further measurement of these compounds at a low temperature would be an interesting subject for future research.

Summary

Continuing our previous studies of the Mössbauer spectra of inorganic iron compounds,[1] we have found some characteristic features of the spectra of some organic iron compounds. There is a general tendency, in a series of related compounds, for the isomer shift and the quadrupole splitting to increase regularly with increase in the structural complexity of the compounds.

The data for iron(III) acetate, benzoate and salicylate suggest the polynuclear structure of these compounds. The observed isomer shifts for other organic iron compounds may also be interpreted in terms of the chemical binding in the molecule.

No resonance absorption was observed for a few groups of organic iron chelates (1, 3 diketone derivatives, etc.). Though our interpretation is still conjectual, the reason for this is believed to rest in the high recoil probability of these compounds.

This work was done at The Institute for Solid State Physics, The University of Tokyo. The authors wish to express their gratitude to Professor Tamotsu Yoshino for his gifts of two samples used in this work. The authors are also indebted to Drs. Kazuo Ôno, Atsuko Ito, Masatake Honda, Shigeru Ohashi, Hideo Yamatera, Masako Shima, Hirotoshi Sano and Kunihiko Mizumachi for their helpful discussions.

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